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Effect of Phenolic Compounds and Resin Acids on the Polymerization of Styrene in the Coexistence of Inhibitors

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禁止物質共存下のスチレン重合における フェノール性化合物と樹脂酸の影響

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要　旨

禁止物質共存下のスチレン重合における，フェノール性化合物と樹脂酸の影響を，ディラトメーターを使用して検討し，次の結果を得た。

1．ヒドロキノン存在下では，ケルセチンとプロトカテク酸エチルが，重合遅延の相乗効果を示した。

2．ヒドロキノンとピロカテコール存在下では，フェノール性化合物の添加により禁止時間は，余り増加しない。

3．ヒドロキノンとピロカテコール存在下では，特に樹脂酸のピペリジン塩フラクションが，禁止時間を短縮する拮抗作用を示し共役二重結合を持つアビエチン酸が原因であろう。

4．非共役樹脂酸であるクリプトピマール酸は，ヒドロキノンの重合遅延に対し，相乗作用を示した。

1．Introduction

Up to the present many studies have been done on the inhibitors for the polymerization of styrene and it has been reported that wood extractives inhibit the polymerization of vinyl monomers.[1] However, the synergistic or competitive inhibition on the polymerization of vinyl monomer has seldom been studied under the condition in the coexistence of inhibitors and added substances. As the synergistic inhibition, Sagawa *et al.* reported that the coexistence of phenolic compounds and the substances having a hetero-atom was effective.[2] In the case of the competitive inhibition the rapid cross termination of radicals which are generated from the two different inhibitors is considered to be effective in the inhibition of the autoxidation.[3]

The purpose of this paper is to investigate the synergistic and competitive inhibition

in the polymerization of styrene by phenolic compounds or resin acids in the presence of quinone, hydroquinone and pyrocatechol. Phenolic compounds investigated are ferulic acid[4] which is reported to be an active constituent in wood extractives inhibiting the polymerization of vinyl monomers, quercetin, syringaldehyde and ethyl protocatechuate. Various resin acids were studied since authors have found that inhibitors become inactive on curing of unsaturated polyester resin varnish with the addition of resin acids.[5]

2. Experimental

Measurement of the polymerization was carried out by dilatometric method as reported previously.[6] Commercial styrene was washed with 10% sodium hydroxide and water successively to remove inhibitors, dried and distilled under the reduced pressure (30 mmHg) at about 55°C with the purified nitrogen-stream immediately before polymerization measurements. Benzoyl peroxide (BPO) used as an inhibitor was recrystallized by dissolving in chloroform and adding to methanol in an acetone-dry ice bath. *p*-Benzoquinone was recrystallized from water, and α-naphthoquinone was recrystallized from ethanol. Hydroquinone and pyrocatechol were used without purification, and ferulic acid, syringaldehyde and ethyl protocatechuate were recrystallized from ethanol.

Total resin acids were isolated by Kajane and Hankanen's method.[7] Commercial rosin (50 g) was dissolved in acetone (250 ml) and an acetone solution (125 ml) of cyclohexylamine (250 g/liter) was added. The precipitate was filtered and washed with acetone at 0°C. The salt was suspended in concentrated boric solution and the resin acids were extracted with ether. The solution was washed with water and dried with sodium sulfate. The ether was evaporated and the product was dried.

Piperidine salt fraction was obtained in the following manner. A solution of 100 g of commercial rosin in 200 ml of *n*-heptane was filtered and 25.5 g of piperidine was added at 45°C. The salt was recrystallized 4 times. The crystals were converted to the free acid by suspending them in 150 ml of acetone and adding 30 ml of 3N hydrochloric acid. The acid was precipitated by adding 200 ml of water, redissolved in 100 ml of acetone and precipitated by water again. The recrystallization from the minimum amount of boiling acetone gave crystals of melting point of 158–160°C.

2-Amino-2-methyl-1, 3-propandiol salt fraction was obtained in the following manner.[8] Commercial rosin (200 g) was dissolved in 700 ml of methyl ethyl ketone. The temperature was raised to 75°C and 60 g of 2-amino-2-methyl-1, 3-propandiol was added with stirring. The solution was allowed to cool to room temperature overnight. The resulting amine was recrystallized from methyl ethyl ketone and coverted to the free acid by suspending in acetone and adding 2N acetic acid to the suspension. The acid was precipitated by adding water until the solution was quite turbid and recrystallized from acetone. The crystals gave the melting point of 154°C.

Cryptopimaric acid extracted from *Juniperus* sp. was offered by Dr. M. Yasue. Total

resin acids, piperidine salt fraction and 2-amino-2-methyl-1, 3-propandiol fraction were acidic in ethanol solution and each of them gave clear violet coloration with Liebermann-Storch test.

The molar ratio of BPO to styrene was 0.004, and that of hydroquinone, α-naphthoquinone and pyrocatechol to BPO was 0.025 in dilatometric measurement at 50°C. At 60°C those of α-naphthoquinone and p-benzoquinone were 0.04 and 0.02, respectively. The molar ratios of ferulic acid, syringaldehyde, quercetin and ethyl protocatechuate to BPO were 0.09, 0.18, 0.0125 and 0.025, respectively at 50°C, those of ferulic acid, quercetin and ethyl protocatechuate being 0.18, 0.025 and 0.09, respectively at 60°C. Hydroquinone, ferulic acid and quercetin were partly insoluble in styrene and other substances were soluble.

3. Results and Discussion

3.1 Effect of Phenolic Compounds

3.1.1 Hydroquinone and Quinone System

An inhibitor is defined as a substance which can react with a radical to form products incapable of adding monomer. If the inhibitor is very effective, no polymer may be formed; the difference between the inhibition and retardation is merely one of degree.

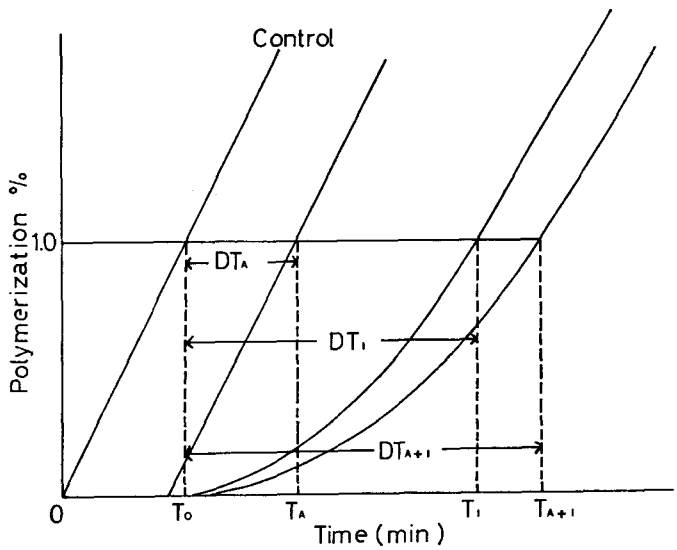

Fig 1. Evaluation of delay time(DT) to 1.0% conversion

It is considered that three patterns appear in the inhibited polymerization in the coexistence of the different inhibitory substances. They are named as competitive effect, additional effect and synergistic effect, and explained in Figure 1. The delay time (DT) to a given degree of conversion (polymerization) is expressed in values compared to control.

Delay time by the added substances; $DT_A = T_A - T_0$

Delay time by quinone and hydroquinone; $DT_I = T_I - T_0$

Delay time by the coexistence of the two different substances; $DT_{A+I} = T_{A+I} - T_0$

The competitive effect and synergistic effect are difined in this study by equation 1 and 2, respectively.

$$DT_{A+I} < DT_A + DT_I \quad (1) \qquad DT_{A+I} > DT_A + DT_I \quad (2)$$

One percent conversion and 0.01% conversion were used as the indices, since the conversion curve under the inhibitory effect consisted of the induction period and the retardation period. The induction period indicates the time required to the commencement of the polymerization reaction, and the retardation period indicates the time giving the retarded polymerization before the free radical concentration reaches a steady state value. The conversion of 0.01% was used as the measure of the induction period, since it was the measurable limit. The conversion of 1.0% was used as that of the retardation period.

The experiment was carried out in the coexistence of *p*-benzoquinone or *α*-naphthoquinone or hydroquinone with phenolic compounds, and phenolic compounds have the inhibitory effect by themselves. As shown in Table 1 and 2 (DT_A), ferulic acid and syringaldehyde exhibit the inhibitory effect at 50°C. Ethyl protocatechuate and quercetin exhibit the inhibitory effect at both 50°C and 60°C. Therefore the last two have stronger effect than the others. In this experiment the effects of one of these compounds were investigated in the presence of hydroquinone and quinone.

Table 1. Delay Time (min) with Phenolic Compounds at 50°C

	Conversion %	DT_I	Ferulic acid	Syringaldehyde	Quercetin	Ethl protocatechuate
DT_A	0.01	—	39.2	61.4	33.7	52.0
	1.00	—	44.0	62.8	34.0	51.2
Hydroquinone system	0.01	34.5	DT_{A+I}			
			33.2	54.2	55.3	47.4
	1.00	114.6	126.4	140.1	318.0	403.2
Naphtho quinone system	0.01	14.2	18.2	45.3	24.7	65.0
	1.00	104.8	106.0	176.3	137.0	173.0

Table 2. Delay Time (min) with Phenolic Compounds at 60°C

	Conversion %	DT_I	Ferulic acid	Syringaldehyde	Quercetin	Ethyl protocatechuate
DT_A	0.01	—	0	0	17.8	39.0
	1.00	—	0	0	17.0	40.8
Naphthoquinone system	0.01	9.3	DT_{A+I}			
			11.0	9.7	17.2	27.0
	1.00	42.4	44.0	46.6	64.6	119.5
Benzoquinone system	0.01	19.2	—	—	25.6	57.6
	1.00	106.8	—	—	122.2	150.8

The comparison of DT in the case of the addition of ferulic acid or syringaldehyde is listed in Table 1. For ferulic acid DT_{A+I} to 0.01% conversion was almost equal to that of hydroquinone (DT_I). For syringaldehyde DT_{A+I} to 0.01% conversion was shorter than the additive value. In the both cases DT_{A+I} to 0.01% conversion did not show the additive property. In other words the inhibitory powers of the coexisting two inhibitors are compensated each other. It is probable that the rapid cross termination occurs between the radicals of the inhibitors.

The results of the addition of ethyl protocatechuate and quercetin also are listed in Table 1. The rate of the polymerization after the inhibition period decreased remarkably. However, DT_{A+I} to 0.01% conversion was almost equal to or somewhat shorter than the additive value, and these results were in good agreement with those of syringaldehyde and ferulic acid. The retardation may be due to the product formed with the mutual reaction of the inhibitors.

The experimental results of *p*-benzoquinone and α-naphthoquinone are listed in Tables 1 and 2. In the case of *p*-benzoquinone and α-naphthoquinone systems, the retardation effects which were remarkable with quercetin and ethyl protocatechuate in hydroquinone system were not observed. However, DT_{A+I} to 0.01% conversion was almost equal to or somewhat shorter than the additive value similarly to hydroquinone system. Hence it can be considered that if there is any interaction between the different radicals, it does not retard the polymerization significantly. DT_{A+I} to 1.0% conversion was shorter than the additive value only for ferulic acid. Ethyl protocatechuate exhibited the weak synergistic effect in α-naphthoquinone system. The other substances gave the additive value.

3.1.2 Pyrocatechol System

The inhibition of pyrocatechol has a different character from hydroquinone, *p*-benzoquinone and α-naphthoquinone. After the induction period and the retardation disappeared, the approach to the uninhibited rate of polymerization is sharp. In the case of the addition of the substances such as ferulic acid, syringaldehyde, quercetin and ethyl protocatechuate which does not exhibit the retardation, the conversion curve with a sharp inflection point will be expected. The experimental results in the presence of pyrocatechol are shown in Figure 2. The inhibitory effect of pyrocatechol was weakened by the addition of phenolic com-

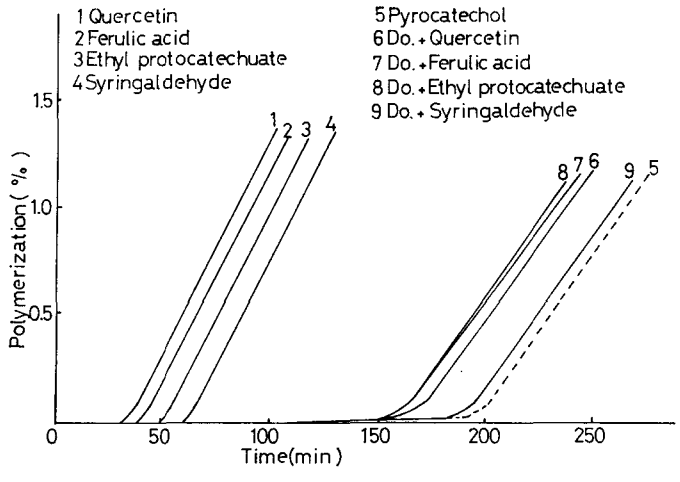

Fig 2. Inhibitory effect of phenolic compounds on the polymerization of styene in the presence of pyrocatechol

pounds, and the time to 1.0% conversion was shortened too. This fact supports the experimental results of 3.1.1, and can be explained from the viewpoint of the rapid cross termination between radicals of the two different inhibitory substances.

$$A\cdot + A'\cdot \rightarrow AA'$$

where A· is the inhibitory radical from pyrocatechol, and A'· the radical from phenolic substance. When this reaction has a faster reaction rate than that of the termination with like radicals, the inhibitory effect decreases with the coexistence of the two different inhibitory substances as seen in this case.

3.2 Effect of Resin Acid

Resin acids are classified into two groups; one is an abietic type with the conjugated double bond, and the other is a pimaric type without that. Resin acids do not affect by themselves the polymerization of styrene. That is, they do not cause the inhibition and retardation, and the rate of the polymerization agrees with that of control. However, resin acids affect the polymerization of styrene when it is added to styrene in the presence of inhibitors. The experimental results of the addition to hydroquinone are shown in Figure 3, where the molar ratio of resin acids to BPO is 0.1. They are divided into the two main classes of synergistic effect and competitive effect. The retardation of polymerization increased with the addition of resin acid without the conjugated double bond such as cryptopimaric acid, which is reported as a mixture of isodextropimaric acid and sandaracopimaric acid.[9] Conversely total resin acids

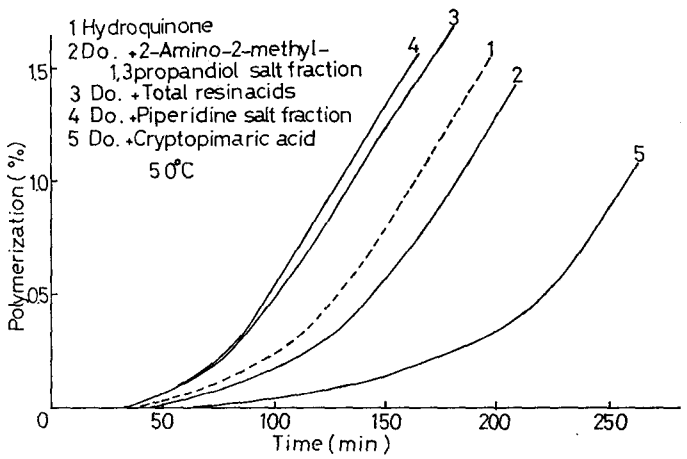

Fig 3. Effect of resin acids on the polymerization of styrene in the presence of hydroquinone

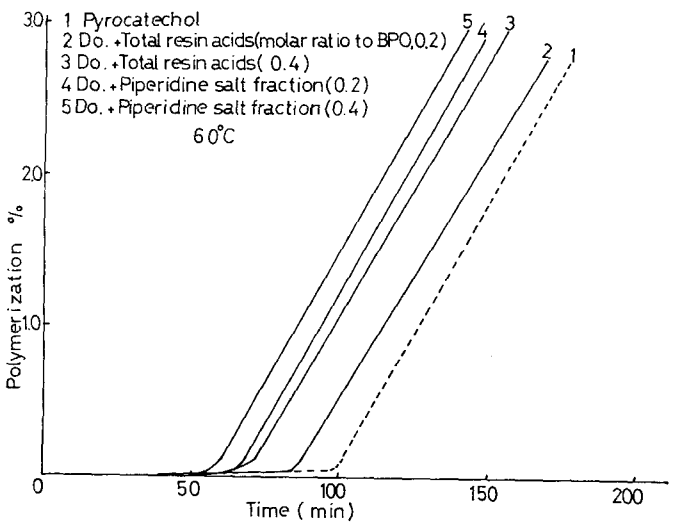

Fig 4. Effect of resin acids on the polymerization of styrene in the presence of pyrocatechol

and resin acid seperated from piperidine salt exhibited the competitive effect. 2-Amino-2-methyl-1, 3-propandiol salt fraction retarded slightly the polymerization.

In UV spectra total resin acids, piperidine salt fraction and 2-amino-2-methyl-1, 3-propandiol salt fraction showed the maximum absorption at 241 nm, 241 nm and 250 nm, respectively. The spectra of piperidine salt fraction agreed with the maximum absorption of abietic acid. Then it suggests that abietic acid is the chief ingredient of the total resin acids. The spectra of 2-amino-2-methyl-1, 3-propandiol fraction agreed with the maximum absorption of neoabietic acid.

The result of the addition of total resin acids and piperidine salt fraction in the case of pyrocatechol system is shown in Figure 4. The molar ratio of pyrocatechol to BPO is 0.05, and the molar ratio of resin acids to BPO are 0.20 and 0.40. The both exhibited the competitive inhibition in the same way as hydroquinone system. The competitive inhibition increased with the increasing amount of total resin acids and piperidine salt fraction. It is assumed from these results that the competitive effect is due to abietic acid and the conjugated double bond existing in the same ring takes part in the effect.

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Résumé

The purpose of this paper is to investigate the synergistic and competitive effects of phenolic compounds and resin acids on the polymerization of styrene in the coexistence of inhibitors, and the results obtained are as follows:

1. Quercetin or ethyl protocatechuate exhibits a synergistic effect of retardation on the polymerization in the presence of hydroquinone.
2. In the presence of hydroquinone or pyrocatechol the induction period does not increase significantly with the addition of phenolic compounds.
3. In the presence of hydroquinone or pyrocatechol total resin acids, specially piperidine salt fraction, exhibit the competitive effect which reduces the induction period. It is considered that abietic acid which has the conjugated double bond takes part in the effect.
4. Cryptopimaric acid which has not the conjugated double bond retards the polymerization remarkably in the presence of hydroquinone.